Fig. 1. Thin section of canyon-wall tuff. Image by the authors.

THE ROLE OF BIOFILMS AND LICHENS IN THE PRESERVATION OF ARCHAEOLOGICAL FEATURES IN THE BANDELIER TUFF, BANDELIER NATIONAL MONUMENT

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Case hardened surfaces that develop over tuff outcrops in Frijoles Canyon (Bandelier National Monument, New Mexico, USA) are a combination of biotic and abiotic crusts that contribute to the preservation of ancient anthropogenic features carved in the cliffs. This study shows that in the initial stages of crust development, lichens and other surface biota cement wind-blown and water-transported particles to the rock face and reinforce and stabilize the accumulated clay / silt coatings. Abiotic crusts form on canyon walls by the partial dissolution of the tuff in the near-surface zone, followed by precipitation of secondary minerals that form a durable cement. We conclude that acid excretions from cyanobacteria and lichens colonizing the surface act to catalyze tuff dissolution. The resulting case hardened surfaces are more erosion resistant than the underlying rock, and protect the fragile prehistoric rock-cut dwellings (cavates), features, and petroglyphs left by the ancient Pueblo people. In conducting the study, researchers have considered whether lichen/biofilm cover may improve bulk mechanical properties of the tuff that outweigh biodeteriorative effects and provide some degree of protection to the material below. These are the initial results of an ongoing project. We hope that better understanding of case hardening / crust formation will lead to the development of low-impact interventions that promote, or at least do not inhibit, natural colonization of the partially hardened surface by lichens and other biota.

Keywords:
tuff – biofilm – lichens – archaeological site – crust – preservation

1. INTRODUCTION

The deeply dissected Pajarito Plateau, located on the eastern flank of the Jemez Mountains of northern New Mexico, is characterized by numerous fingerlike mesas and deep sheer-walled canyons formed from erosion of two thick ignimbrite sheets deposited by separate eruptions approximately 1.6 and 1.2 million years ago (Fig. 2). Ancestral Pueblo people and others have used the plateau for thousands of years, with peaks in population occurring from the 12th to the mid-16th century. Among the most extraordinary of the archaeological sites are the rock-cut caves called cavates (derived from the words "cave" and "excavate"), which were used as dwelling, storage, and special-purpose rooms. They are the ancestral dwellings of the Native American Pueblos that still live in the region (Fig. 3).

The cavates were carved directly into the soft rhyolitic tuff, along a weakly cemented zone where the two ash flows meet. There are a few thousand of these dwellings on the Plateau in an area of about 620 square kilometers. Many of these have intact earthen wall plasters and floors, some with polychrome and incised decoration, as well as numerous built-in features to produce and store food and to weave fabric (Fig. 4). The landscape surrounding the cavates is full of architectural and agricultural artifacts, including multi-story masonry community houses, foot trails worn in

Fig. 2. Frijoles Canyon in Bandelier National Monument, where there are over 1000 cavates in a 2 km-long section of the canyon. The mountains in the background give the general location of the Toledo and Valles calderas that spewed ash forming the Bandelier Tuff approximately 1.6 and 1.2 million years ago. Over 300,000 people a year visit this canyon to explore the cavates.

the tuff, water collection and transport systems, stone shrines, and painted incised symbols (also known as petroglyphs) on the cliff faces and plastered walls. Bandelier National Monument is located in Frijoles Canyon, one of the longest and deepest canyons on the plateau, and has been a National Monument since 1916.

One challenge of conserving the cavates is how to preserve their physical integrity despite constant landscape-level change and erosion of the cliffs (Fig. 5). Deterioration processes affecting cavate condition include mass wasting of the cliff face through losses of fracture-bound boulders, mechanical damage of outcrop surfaces, the interaction of the tuff with wind and water, and the presence (or not) of a weather rind or case hardened surface on the tuff outcrops. Case hardening appears to protect the glassy ash of the Qbt1g unit (the cooling unit in which most of the cavates are carved) from erosion and loss, at least partially as the result of secondary minerals deposited in near-surface pore spaces. Weather rind formation begins with the deposition of dissolved solutes and suspended particulates on rock surfaces by surface water flowing over canyon walls, followed by the colonization of the rock surface by surface-stabilizing

Fig. 3. Long House Pueblo at Bandelier National Monument. From the visitor trail one can see cavates carved into the poorly consolidated Qbt1g subunit of the Bandelier Tuff, along with viga sockets that supported wood roof members in the masonry rooms that formed the front of the pueblo. These rooms are in ruins (photo foreground), and earthen plasters that finished the room interiors is visible on the outcrop surface (below the viga sockets). Note the case-hardened surfaces, especially on the upper right; this research is focused on the processes of their formation. Photo credit: Western Mapping Co.

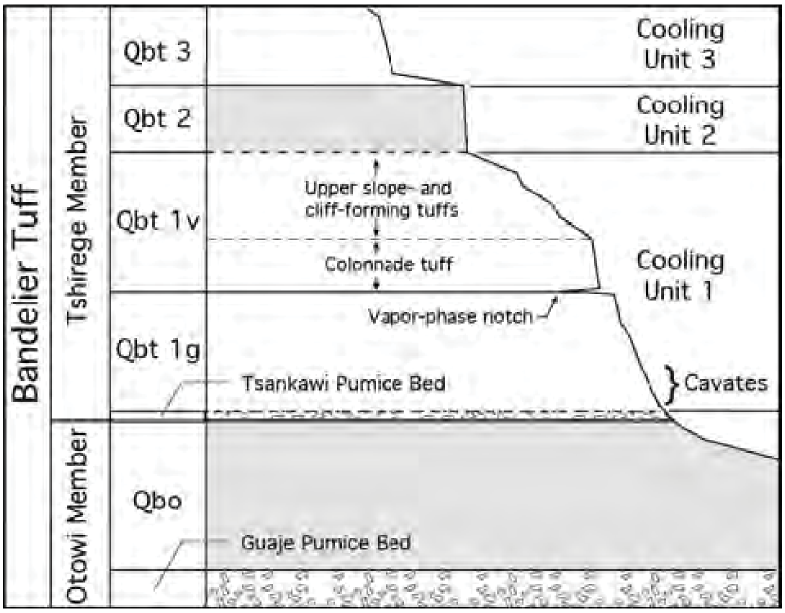
Fig. 4. Inside the cavates are numerous built-in features to produce and store food and to weave fabric. This is the only place where the domestic details of the lives of the prehistoric Pueblo people are still visible. Cavate interiors are often sooted and plastered with up to 30 layers earthen plaster, some of them decorated with painted and incised designs.

biota that include cyanobacteria and lichens. The growth of lichens and other biotic crust constituents on exposed surfaces is especially important for promoting development of case hardening by catalyzing bio-geochemical reactions that lead to dissolution of the volcanic glass and precipitation of secondary minerals in the near-surface zone.

Biodeteriorative effects of lichens and other biota on rock surfaces, and particularly on rock art and monuments of rock or stone, are well documented (e.g., COOKS & FOURIE, 1990; STRETCH & VILES, 2002; SOUZA-EGIPSY et al., 2004; GORDON & DORN, 2005). As a consequence, design responses from the heritage community are typically focused on removal (CANEVA et al., 2008; SCHEERER et al., 2009). Lichens and biofilm constituents absorb water and produce weak acids that increase the solubility of rock surfaces and result in modifications of the mineral substrata. Lichen hyphae and rhizines exploit naturally occurring fractures in the rock, lichen thalli expand and contract with changes in temperature and humidity, causing exfoliation of the substrate surface in the process, and produce organic salts that are also expansive.

Fig. 5. Cavate B002 with its surviving masonry wall (bottom center). Note the broad range of case hardened surfaces of the surrounding tuff, and the "swiss-cheese" texture that develops where the durable case hardened surface is breached, exposing the soft underlying tuffs to erosion. The extensively altered surfaces (upper half) are types 6 and 7 (see Table 1); on the far right a more recently exposed surface, slightly recessed and having a smoother texture, has developed another rind. Areas of recent erosion appear as white or grey patches (Type 1); erosion at the lower right edge of the cavate threatens to undermine the prehistoric wall. Some of the freshly exposed tuff has begun to acquire silt-clay coatings (Type 2) that constitute one of the initial stages of case hardening. At bottom left, moderately well indurated surfaces have silt-clay layers colonized by lichens and other microflora (which appear yellow, green and black in the photo). Note the partially detached boulder above the wall, the column of cantilevered stones at the east end of the surviving wall, and the erosion of the tuff just below this column.

Fig. 6. Schematic stratigraphic column for the Bandelier Tuff showing subunits of the Tshirege Member in the ruins area of Frijoles Canyon.



Damage associated with these processes, which include depletion of structural cations, fragmentation and dissolution of small grains, surface staining, disintegration, and exfoliation was once thought to occur very slowly, but recent research indicates that some rocks and building stones are significantly impacted in a decade or less.

However, under some circumstances lichens may provide a level of weather protection to relatively porous and unconsolidated rock substrata. This appears to be particularly true of the Bandelier Tuff, where lichen cover actually seems to improve the weather resistance of the tuff and provide some degree of protection to archaeological resources carved in the rock. In this case the lichen cover seems to function more like a biological soil crust, forming a barrier layer shielding rock surfaces from water flow, wind abrasion, and temperature variation, resulting in reduced weathering rates.

2. TUFF STRATIGRAPHY AND CHARACTERIZATION

The Bandelier Tuff consists of two regional rhyolitic ignimbrite sheets, the Otowi and Tshirege Members. These tuffs were erupted 1.61 and 1.22 Ma ago, respectively, from the Valles caldera complex in the central part of the Jemez Mountains volcanic field (SMITH & BAILEY, 1966; SMITH et al., 1970; IZETT & OBRADOVICH, 1994; SPELL et al., 1996). The Otowi Member consists of poorly indurated non-welded tuffs that form talus-covered slopes at the base of Frijoles Canyon. The Tshirege Member is a multiple-flow ignimbrite that forms the prominent canyon walls in Frijoles Canyon. The Tshirege Member has a complex welding profile that results in dramatic cliffs separated by narrow benches, and is subdivided into mappable cooling units that reflect the complex emplacement and cooling history of the tuff (SMITH, 1960a and 1960b, SMITH & BAILEY, 1966; CROWE et al., 1978, BROXTON & RENEAU, 1995). In the study area, three cooling units are recognized based on welding compaction and crystallization zones (Fig. 6). The zonal patterns of welding and crystallization produce vertical variations in density, porosity, hardness, and color that are reflected in the canyon wall profile, particularly on arid south- and southwest-facing canyon walls that receive daily sun exposure year-round.

The Tshirege Member is approximately 134 m thick near the park's visitor center. Approximately 95% of the Pueblo archaeological fabric occurs in the non-welded vitric tuffs that make up the lower 21 m of the Tshirege Member. These tuffs are shown as unit Qbt 1g in Fig. 5. Although tuffs of unit Qbt 1g are generally soft, they commonly form near-vertical cliffs because they are capped by strongly indurated welded tuffs higher on the canyon walls. Unaltered tuffs near the base of unit Qbt 1g are white but gradually become light pinkish-orange and slightly more indurated up section. Qbt 1g tuffs consist of pumice lapilli >2 mm in size in a poorly sorted matrix of ash, crystals, and rock fragments (BROXTON & RENEAU, 1995).

The mineralogy of unit Qbt 1g is dominated by 60- to 70 wt. % volcanic glass that occurs as pumices,

Fig. 7. Edge of an erosional remnant of a Type 7 case hardened surface showing a more recently exposed adjacent surface (left) that is less altered.

Fig. 8. Case hardened surfaces in unit Qbt 1g of the Tshirege Member of the Bandlier Tuff. 'Swiss-cheese' texture is characteristic where holes develop in the durable case hardened surface, exposing the soft underlying tuffs to preferential erosion by wind and water.

shards, and ash[1] (BROXTON et al., 1995). The absence of significant secondary minerals in the glass, such as clays and zeolites, strongly suggests that these tuffs have had limited contact with groundwater since their deposition. Crystalline components of the tuff are primarily sanidine and quartz phenocrysts; subordinate clinopyroxene, hornblende, and fayalite phenocrysts; and trace magnetite, zircon, and chevkinite microphenocrysts. Crystalline lithic clasts of reddish-brown-to-black porphyritic dacite and crystal-poor devitrified welded tuff are generally sparse (<1%). Unaltered tuffs in unit Qbt 1g have an average matrix porosity of 46% and an average dry bulk density of 1.26 gm/cm3 (ROGERS & GALLAHER, 1995). Porosity in these tuffs includes intergrannular pore spaces between particles and vesicles in pumice clasts. Pumice vesicles include highly inflated equant varieties and bundles of stretched tubes.

Many Qbt 1 canyon wall exposures are covered by pale-orange case hardened surfaces that are 0.25 to 1.3 cm thick. These surfaces are resistant to erosion and form a protective layer over the underlying softer tuffs (Fig. 7). Some of the anthropogenic features, like petroglyphs and hand-and-toe-hold trails carved into the outcrops 500-1000 years ago, have case hardened surfaces. The case hardened surfaces commonly have a distinctive "swiss cheese" appearance where round to elliptical cavernous hollows penetrate the hard surface layer, exposing underlying softer tuffs to selective erosion by wind and water (Fig. 8; cf. Fig. 5). The degree of case hardening varies from location to location, resulting in differential weathering patterns on cliff faces. For this study, a scale was developed to describe the progressive development of case hardening on cliff faces (Table 1). The scale includes seven categories of case hardened surfaces with Type 1 representing the least altered surfaces (fresh tuff)

[1] *This paper differentiates between fine (0.001-0.01 mm) and coarse volcanic ash (0.01-2 mm) because of the different behaviors associated with these particle sizes during alteration. We call coarse ash particles shards. Shards are large enough to contain vesicles and preserve delicate cuspate forms that are the junctions of two or more vesicles.*

Type 1		• Freshly exposed, apparently unaltered tuff • White to light gray in color • Rough texture with prominent pumices • Little to no sedimentation of silt-clay or calcite visible on surface • Easily abraded with light pressure • Fine glassy ash in the tuff matrix is abundant and unaltered • Matrix porosity is high (40-50%) • Secondary minerals are absent to rare
Type 2		• Sedimented silt-clay coating over freshly exposed tuff • Coating is very thin, resembling a wash, and is often in runnels down the tuff surface • Filamentous cyanobacteria frequently found to have colonized this surface coating • Fine glassy ash in the tuff matrix is abundant and unaltered • Matrix porosity is high (40-50%) • Secondary minerals are absent to rare
Type 3		• Black biofilm layer overlaying exposed tuff • Silt-clay coating / lichen cover are less prominent surface features • Moderately indurated and resistant to erosion • Alteration is sporadic and generally limited to a zone 0.1 to 0.5 cm thick • Porosity remains high where the tuff is little altered, but in heavily mineralized areas is reduced to 20 to 30%
Type 4		• Lichens and other biogrowth appear over a prominent silt-clay coating • Crustose lichens are more plentiful than in other surface types • Moderately indurated and resistant to erosion • Alteration is sporadic and generally limited to a zone 0.1 to 0.5 cm thick • Porosity remains high where the tuff is little altered, but in heavily mineralized areas is reduced to 20 to 30%
Type 5		• Generous lichen distribution, often accompanying a thick silt-clay coating • Comparatively smooth texture, lacking the large surface asperities that are typical of Types 6 and 7 • Moderately indurated and resistant to erosion • Alteration is sporadic and generally limited to a zone 0.1 to 0.5 cm thick • Porosity remains high where the tuff is little altered, but in heavily mineralized areas is reduced to 20 to 30%

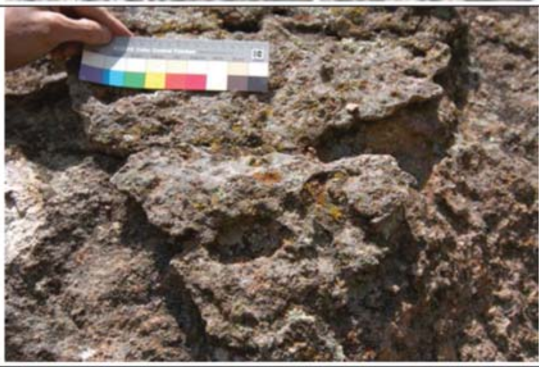
Type 6		• Well developed lichen growth • Surface is rough, with asperities in the range of 1-3cm • Abrupt changes in surface level at losses, with crust thickness of up to 4 cm • Strongly indurated, with crusts that are generally 1 to 1.3 cm thick • Case hardened zone is commonly made up of two parallel bands of alteration • Porosity for the inner alteration band commonly <5%
Type 7		• Well developed lichen growth, with greater biocommunity diversity • Severely eroded, with surface asperities in the range of 1-6cm • Examples have prominent edges with crust thickness of up to 6 cm • Strongly indurated, with crusts that are generally 1 to 1.3 cm thick • Case hardened zone is commonly made up of two parallel bands of alteration • Porosity for the inner alteration band commonly <5%

Table 1. Tuff surface types.

and Type 7 representing the most altered surfaces. Classification of case hardened surfaces is based on observations about the thicknesses and hardness of altered surfaces, color, surface roughness, and the abundance and diversity of surface biota (mostly lichens). Samples for this study were selected to represent the various stages of development of these surfaces.

Canyon walls are continually modified by cliff retreat processes such as rock falls and large-block failures. These gravity-driven processes, which play a major role in canyon widening over time, occur when the lithostatic forces acting on a portion of the canyon wall overcome the tensile strength of the tuff, causing it to collapse outward into the unconfined space of the canyon. High-angle fractures in the tuff often act as failure planes, particularly in the tuff units that overlie unit Qbt 1g. These tuff units are strongly welded and contain a dense network of cooling fractures along with some tectonic fractures. Unit Qbt 1g has fewer fractures because it was emplaced at lower temperatures and did not develop cooling fractures. Despite having relatively few fractures, there are locations where Qbt 1g rock falls or large block failures were controlled by high-angle fractures (RENEAU, 2000).

Fig. 9. The case hardened tuff surface (left) includes a silt-clay layer colonized by lichens. Note the similarities in surface topography and patina to the biological soil crust on the right.

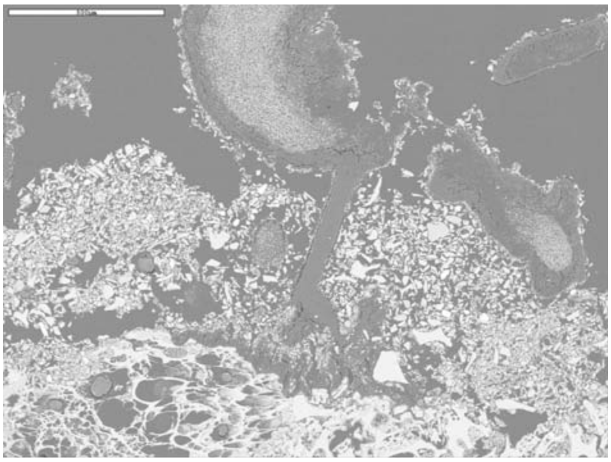


Fig. 10. SEM backscatter image showing a lichen thallus on sedimented volcanic ash adhering to the canyon wall. The lichen is the dark mass at the top. The sedimented layer (middle zone) is over 500 µm thick and includes shards, ash, and crystal fragments embedded in a clay matrix. Lichen rhizines / hyphae (microfilaments) pervade the sedimented layer and help stabilize it. The canyon wall bedrock is the area with the large pumice at the bottom.

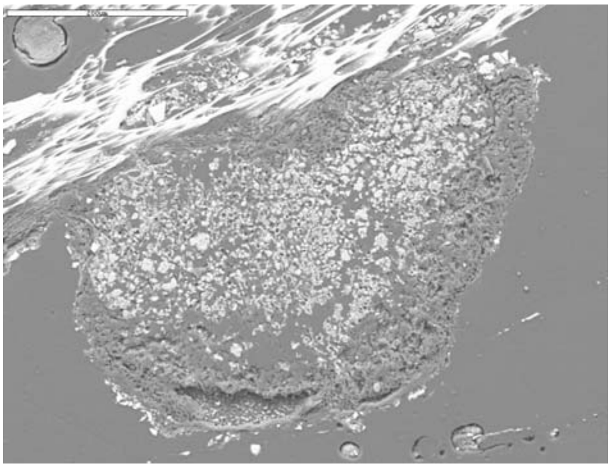


Fig. 11. SEM backscatter image showing a lichen thallus growing directly on tuff on the canyon wall. The lichen is the dark mass with the cellular structure. Light gray crystals of weddellite (calcium oxalate) fill the thallus. Microfilaments invade the long-tube pumice vesicles of the bedrock tuff at the top of the photograph.

In addition to cliff retreat processes, canyon walls are modified by water and wind erosion. Runoff from mesa tops periodically cascades down canyon walls, particularly during monsoonal rainstorms that are common during the summer months. Sheet flow of surface water over exposed cliff faces dislodges and transports loose particles. Drainages on mesa tops often funnel runoff to particular areas of the canyon wall, eroding deeply recessed slots and alcoves that contain pour-offs. Discharge of large volumes of sediment-laden water in these canyon wall drainages greatly accelerates erosion at these locations. During cold-weather months, near-surface tuffs and fractures periodically become saturated locally due to imbibition of snowmelt and runoff; these tuffs are susceptible to mechanical disaggregation by freeze/thaw cycles. Wind erosion also plays a role in modifying canyon walls, forming erosional features on cliff surfaces. Wind-driven particulates sandblast tuff surfaces and contribute to their mechanical disintegration by dislodging and removing the fine ash. Non-welded vitric tuffs are particularly susceptible to erosion because of their low degree of consolidation. Where the case hardened surface is breached, air currents excavate cavernous hollows in the underlying soft tuffs.

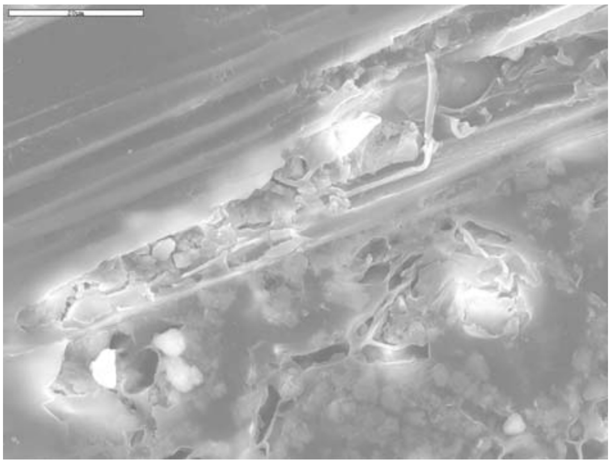


Fig. 12. SEM secondary electron image showing dissolution of pumice vesicle walls in contact with lichen hyphae. The tubular pumice (extending from lower left to upper right) has scalloped edges. Lichen (lower right) is in contact with the pumice and hyphal filaments invade the large open vesicle (upper right).

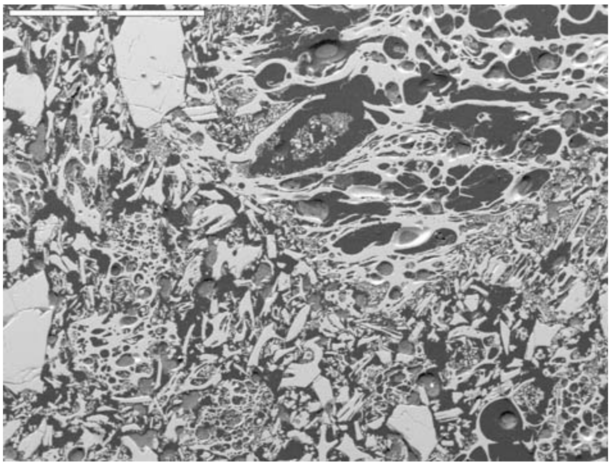


Fig. 13. SEM backscatter image of canyon wall tuff bedrock with Type 1 to 2 alteration. The tuff has undergone minimal alteration and lacks cementation by secondary minerals. The tuff contains abundant vitric ash in the groundmass, and delicate shard and pumice lapilli structures are well preserved. The porosity of the tuff is 40 to 50%.

3. COATINGS AND RINDS

Modification of canyon wall surfaces and development of a hard surface coating or rind (case hardening) involves three main components. 1) deposition of sedimented particulates on exposed tuff surfaces; 2) growth of lichens and microflora on (and in) exposed tuff surfaces and on the sedimented layers that coat them; and 3) bio-geochemical reactions that lead to the dissolution of volcanic glass and precipitation of secondary minerals (Fig. 9).

Thin discontinuous coatings of sedimented particles occur on tuff bedrock surfaces in all seven types of surfaces described in Table 1. Sediment, soil, and tuff particles from mesa tops and canyon walls are mobilized by surface runoff during storm events; as surface-water flow diminishes, a thin coating of clay and silt is deposited on canyon walls. The sedimented layers (0.05 to 0.5 mm thick) are primarily made up of silt-sized (5-50 µm) pyroclasts of glass shards and pumice fragments, subordinate fragments of sanidine and quartz crystals, and traces of oxides such as magnetite and ilmenite. These constituents are common components of Bandelier Tuff and were derived from local sources. Most silt and clay layers show little sorting or layering, though stratified layers in a few samples indicate multiple episodes of deposition. The pyroclasts and crystals are embedded in a matrix of clay-sized particles that cement and stabilize these deposits. SEM EDS analyses indicate the clay minerals are likely smectite and lesser amounts of illite. In some of the more highly altered samples, opal ± clay is the cementing agent for these deposits, with opal cement occasionally concentrated at the interface between the clay-silt layer and the tuff bedrock. Except where cemented by opal, the thin layers of silt and clay adhering to the tuff are too thin, discontinuous, and poorly cemented to significantly impede erosion processes. However, these layers provide a suitable substrate for microflora to colonize canyon walls[2].

Lichens are found on most tuff surfaces[3] and their abundance and diversity appear to increase along with the degree of case hardening. SEM images show that lichens grow on top of the sedimented layers (Fig. 10) as well as on bare bedrock surfaces (Fig. 11). In the Qbt 1g subunit, lichens and other biotic crust constituents help stabilize canyon walls by acting as a protective buffer between the tuffs and wind and surface water erosion and they trap wind-blown and water-transported silt particles within their overlapping lobes. Secretions of sticky polysaccharides enhance cementation of the friable materials found at the substrate surface[4]. Lichen rhizines form a dense network of filaments that invade, reinforce, and stabilize the sedimented layers and the open intergranular pores and pumice vesicles of the bedrock tuff (Fig. 12); in the samples examined for this study, microfungal filaments were found to extend up to 1 mm into the tuff bedrock. Oxalic acid excreted by biotic constituents plays a role in the dissolution of volcanic glass. The role of lichens as a source of oxalic acid is demonstrated by dense accumulations of 1 to 3 µm oxalate crystals in lichen thalli. These crystals are identified as weddellite ($CaC_2O_4 \bullet 2H_2O$) based on their tabular form and SEM EDS analyses. Glass dissolution at the thallus-substrate interface is manifested as scalloped and embayed edges on glass shards and pumice lapilli (Fig. 13).

The growth of lichens and other biocommunity constituents on outcrop surfaces seems especially important for promoting development of case hardening by catalyzing biogeochemical reactions that lead to dissolution of the volcanic glass and precipitation of secondary minerals (BROXTON et al 2014). Microbial activity often results in the acidification of the surrounding habitat (NASH, 2008); for example, accumulation and excretion of tricarboxylic acid pathway metabolites is widespread in fungi (GOLDBERG et al., 2006). These byproducts, particularly oxalic and citric acids, are linked to the dissolution of inorganic substrates necessary for fungal growth (DUTTON & EVANS, 1996; SAND, 1996; CHEN et al., 2000; GADD, 2004, 2007; GUGGIARI et al., 2011). Further, the most reactive of these acids, oxalic acid, has been associated positively with carbon accumulation (JACOBS et al., 2002 and 2004; GIBSON & MITCHELL, 2004; MARTIN et al., 2012) and likely plays an important role in the dissolution of volcanic glass and precipitation of secondary minerals. Primary chemical processes by which lichens solubilize minerals are: 1) generation of respiratory CO_2; 2) the excretion

[2] *In collecting samples of the sedimented clay-silt deposits, researchers have recovered large filamentous cyanobacteria from the coatings.*

[3] *Lichens identified by investigators include* Aspicilia *sp.,* Lecanora *sp.,* Acarospora chlorophana, Staurothele *sp.* Pleopsidium chlorophana, Candellariella rosulans, *and* Toninnia *sp. The development of biotic crusts on anthropogenic features like hand- and toe-holds and petroglyphs indicates that fairly well developed crusts can appear within a few hundred years of exposure.*

[4] *Polysaccharides secreted by soil crust constituents are successful in trapping aeolian material, creating a thin layer of silt and clay on the crust surface that is a nearly ubiquitous feature of the crusts (DANIN & GANOR, 1991; DAVEY & CLARKE, 1992; VERRECCHIA et al., 1995).*

of oxalic acid; and 3) the production of biochemical compounds with complexing ability (CHEN et al., 2000; PINNA, 2014). Secondary processes include citric acid as a chelator and phenolic compounds which act as antimicrobials for self-defense.

Progressive alteration of the glassy components of the tuffs at the canyon wall interface leads to case hardened surfaces that are more durable and less porous over time. The seven surface types described in Table 1 represent a continuum of alteration, and there is considerable overlap between each of the identified types. The least altered canyon surfaces (e.g. Types 1 and 2) are associated with recent rock falls and other fresh exposures of tuff; these are interpreted as the youngest canyon wall surfaces. The most highly-altered surfaces (e.g. Types 6 and 7) are erosional remnants of surfaces that once covered larger areas; these surfaces stand in bas-relief 1 to 6 cm higher than adjacent wall surfaces that are significantly less altered. These characteristics suggest Type 6 and 7 surfaces are the oldest and most stable parts of the canyon wall. Removal of Type 6 and 7 surfaces by rock falls and other mechanisms exposes fresh tuff that begins the process of case hardening anew. The walls of Frijoles Canyon undergo continual modification by erosion and cliff retreat, but these processes do not occur uniformly at all locations. As a result, present-day canyon walls are a mosaic of surfaces that represent various exposure periods and stages of weathering.

Canyon walls with Type 1 and 2 surfaces (Table 1) are the least altered and least durable. Pyroclasts in these tuffs show little or no evidence for glass dissolution and secondary minerals cementing the soft tuff matrix are rare to absent (Fig. 13). In one sample, small amounts of intergrown opal ($SiO_2 \bullet nH_2O$) and smectite group minerals $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \bullet 4H_2O$ are deposited in pores near the outer wall surface, but most of the sample is free of alteration. Important characteristics of Type 1 and 2 surfaces are: 1) fine glassy ash in the tuff matrix is abundant and unaltered; 2) the matrix porosity is high (40-50%); 3) secondary minerals are absent to rare; and 4) exposed tuff surfaces are soft and friable because of the lack of cementation.

Canyon walls with Type 3 through 5 surfaces (Table 1) are moderately indurated and resistant to erosion. Lichens and other biota are abundant on these surfaces and their root systems extend up to 1 mm into the tuff. Dissolution of volcanic glass and deposition of secondary minerals generally occurs in a zone 0.1 to 0.5 cm thick adjacent to the canyon wall. Beyond this zone, secondary minerals are absent and the tuffs show little evidence of alteration. Thin sections examined by optical microscope and SEM show that alteration of the tuff is not uniformly distributed throughout the case hardened zone, and there is significant heterogeneity in the distribution of secondary minerals. This results in enclaves of tuff with few or no secondary minerals interspersed with areas that are thoroughly mineralized. Alteration is largely concentrated in the fine ashy matrix of the tuff where glassy pyroclasts in contact with pore water underwent hydrolysis. Pore water in this near surface environment is recharged by infiltrated surface water, and near-saturation

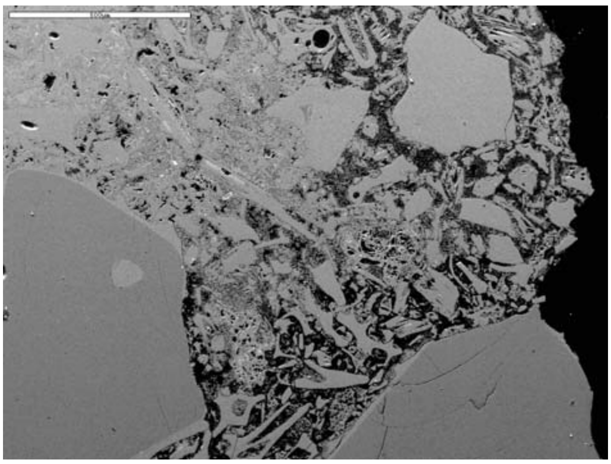


Fig. 14. SEM backscatter image of case hardened tuff with Type 3 to 5 alteration. At the sample surface (right), the larger glass shards are moderately scalloped and unfilled pore spaces still account for 30-40% of the sample volume. Moving left, there is more dissolution and replacement of the original material and pore space is reduced to < 20%. Opal is the dominant filling material; other filling materials include sepiolite and intergrown calcite and opal (4-4). At the far left, open pore space is less than 5% at a depth of approx. 1.30mm.

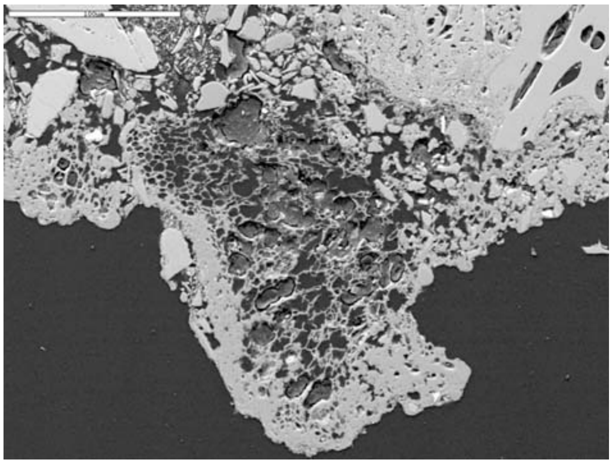


Fig. 15. SEM backscatter image showing pseudomorph of a lichen replaced by opal in a case-hardened surface; delicate cellular structure of lichen is preserved by the mineralization. The lichen is attached to tuff bedrock where most of the fine ash in the matrix is replaced by intergrown opal and clay. Small bright white areas are trace barite.

Fig. 16. Canyon-wall tuff with Type 7 alteration. The image is a thin section butt 2.5 cm wide cut perpendicular to the canyon wall. The canyon wall is on the right side of the image. The case hardened zone is made up of two parallel bands of alteration. The outer alteration band, next to the canyon wall, is mostly white in color. The inner alteration band ranges is medium to dark brown in color. Both bands are extensively altered, but the inner band is more highly mineralized. The tuff left of the inner band of alteration is slightly altered and contains abundant volcanic glass. Porosity is 20 to 30% in the outer band, 1 to 15% in the inner band, and 30 to 40% in the slightly altered tuff.

conditions occurred in some pore spaces for at least short periods of time. Organic acids released by the lichens are almost certainly an important catalyst for hydrolysis reactions by reducing the pH of pore water. Following dissolution, secondary minerals were deposited in open pores, cementing the tuff matrix. Secondary minerals are largely concentrated in the fine-grain groundmass of the tuff and largely replaced fine ash particles (Fig. 14). Larger pyroclasts such as shards and pumice lapilli remain abundant in the alteration zone, but many show moderate to severe dissolution along their margins. Except for oxidation halos around magnetite, crystalline components of the tuff such as phenocrysts and lithic fragments show no apparent alteration. Optical petrography and analyses by microprobe and SEM EDS identify the primary secondary minerals as opal ($SiO_2 \bullet nH_2O$) and sepiolite ($Mg_4(Si_6O_{15})(OH)_2 \bullet 6H_2O$). Calcite ($CaCO_3$) and smectite-group minerals are subordinate secondary minerals and barite ($BaSO_4$) is relatively rare. Texturally, the secondary minerals are intergrown and were apparently co-precipitated. Opal not only

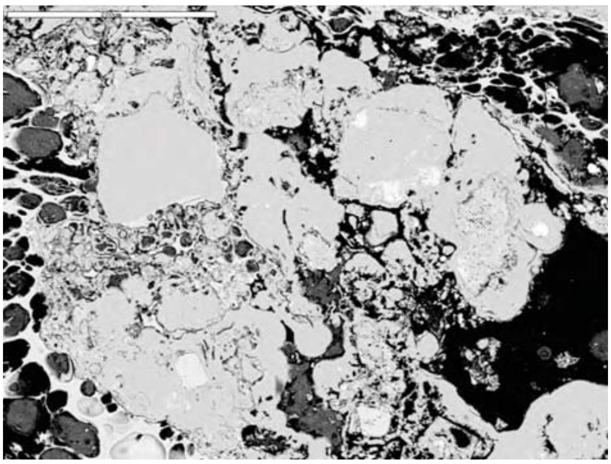


Fig. 17. SEM backscatter image for the outer band of alteration in Type 7 case hardened tuff. Volcanic ash in the tuff matrix is replaced by thick, massive bands of opal (medium gray) and finely intergrown opal and clays (mottled appearance). Some larger glassy pyroclasts (vesicular pumice and 100-µm-wide equant clast in the upper left quadrant) survived alteration, but show moderate to severe effects of dissolution at their margins. There are thin rinds of opal pseudomorphs replacing pumice vesicles in the center left part of the image.

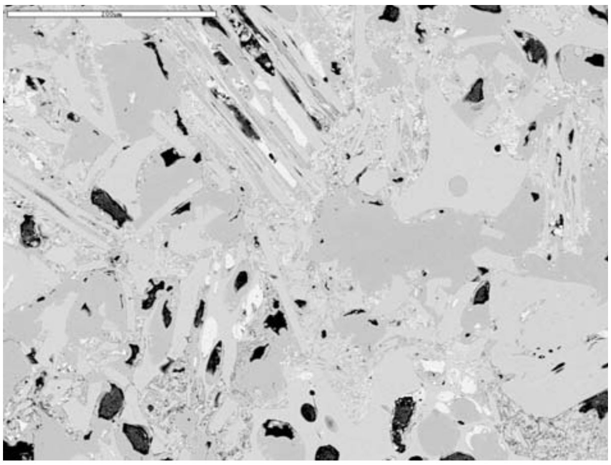


Fig. 18. SEM backscatter image for the inner band of alteration in Type 7 case hardened tuff. Large glassy shards (light gray) show few delicate cuspate structures due to dissolution. The shards are thoroughly cemented by massive opal (medium gray), calcite (white), and sepiolite (small mottled dark gray areas). All of the fine matrix ash and most of the original pore space have been replaced by mineralization. The few remaining pores are shown in black. Image analysis of this image yields the following proportions: 49.2% glass shards, 43% opal, 4.3% calcite, trace sepiolite, and 3.5% porosity.

co-precipitated with other secondary minerals, it also formed thick, optically continuous deposits in pores as a late stage mineral. Botryoidal and rhythmically layered opal lining open vugs suggest that mineralization occurred under saturated conditions. In some samples, lichen thalli adhering to the tuff surface are silicified to opal, preserving delicate structures as pseudomorphs (Fig. 15). Similarly, lichen rhizines / rhyzoids that penetrate the tuff are sometimes replaced by opal, preserving their delicate structures. The porosity of Type 3 through 5 surfaces decreases as the abundance of secondary mineral cements increases. Porosity remains high where the tuff is little altered, but in heavily mineralized areas the porosity is reduced to 20 to 30%.

Canyon walls with Type 6 and 7 surfaces (Table 1 and Fig. 6) are strongly indurated and form the most erosion-resistant cliff faces in unit Qbt 1g. These surfaces are extremely rough and support extensive biocommunities. Case hardened surfaces form crusts that are generally 1 to 1.3 cm thick, but pockets of alteration extend as much as 2.5 cm from the canyon wall. The case hardened zone is commonly made up of two parallel bands of alteration (Fig. 15). The outer alteration band, next to the canyon wall, is 3.5-6.7 mm thick and is mostly white in color. The inner alteration band ranges 5 to 8.5 mm thick and is medium to dark brown in color. The transition between the two zones is abrupt, occurring over a distance of 0.1 mm or less. The outer band is extensively altered, and is characterized by replacement of the ashy tuff matrix by opal that envelops glass shards and pumice lapilli (Fig. 17). The edges of shards and pumice lapilli show moderate to severe dissolution effects. Some of the opal shows rhythmic growth layering. Subordinate to trace amounts of aluminum-rich clay minerals and calcite are intergrown with opal. These secondary minerals form a durable cement that fills a significant amount of the available pore space. Porosity estimates for the outer band of alteration ranges from 20 to 30%. The inner band of alteration is more strongly mineralized than the outer band. Secondary minerals in the inner band of alteration consist of massive opal with intergrown calcite ± sepiolite. Locally, sepiolite and calcite are the dominant secondary minerals. All of the fine ash in the tuff matrix is replaced by massive deposits of secondary minerals that envelop the surviving glass shards and pumice lapilli (Fig. 18). Many of the surviving shards and pumice lapilli are extensively modified by dissolution, but some delicate cuspate shards are surprisingly well preserved. Porosity for the inner alteration band was estimated by image analysis of SEM backscatter images, and ranges from 1 to 15% and was commonly <5%. The transition from the inner alteration band to deeper tuffs (i.e. more than about 1.3 cm from the canyon wall) is marked by a gradual decline in mineralization. As the alteration diminishes, glassy ash in the tuff matrix becomes more prevalent. Porosities in these slightly altered tuffs range from 30 to 40%.

4. WATER ABSORPTION, EROSION RESISTANCE, AND ENZYMATIC ACTIVITY

To characterize the effects of case hardening on the weather resistance of tuff surfaces, a series of tests for

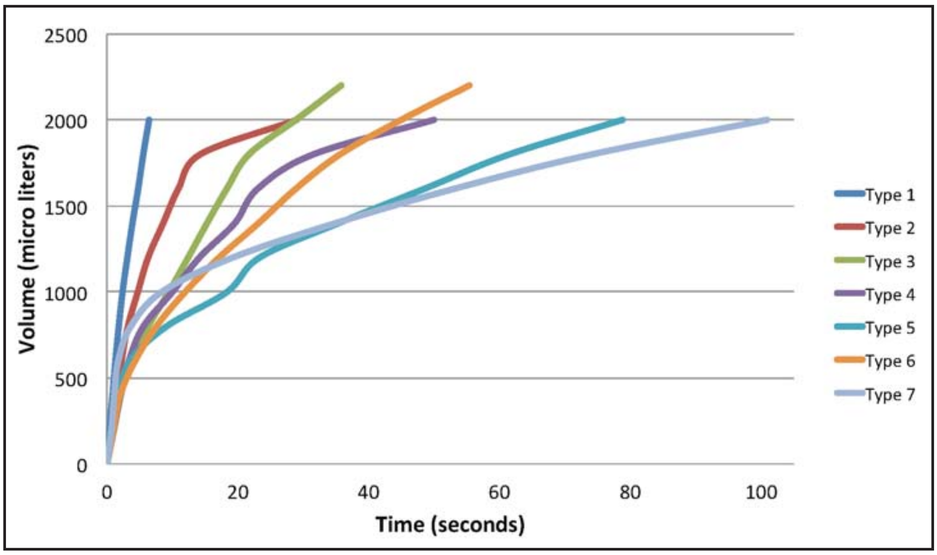


Table 2. Absorption values for each surface type are plotted against time. For Type 1 surfaces the average rate is essentially linear, while for Types 2-7 rates slowed significantly as the experiment progressed.

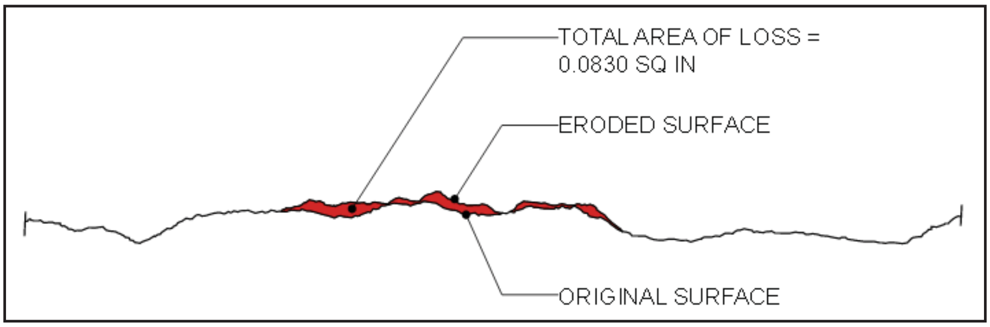


Fig. 19. Sample profile. Image by the authors.

in situ measurement of absorption, erosion resistance to wind and water erosion, and gas permeability were developed and carried out in a pilot project (involving a limited number of samples) conducted in 2013. In addition, a series of enzyme assays, intended to correlate these properties to enzymatic activity, were conducted in the laboratory. As has been noted, alteration of the tuff in the near-surface zone is discontinuous, especially for case hardened surfaces that are less well developed, so measurements display a broad range of values.

To test the hypothesis that pore filling minerals and mucilaginous cyanobacteria in crusts that develop on the rock surface reduce the water uptake of the porous rock, investigators collected measurements using a prototype device developed by the Institute for Theoretical and Applied Mechanics (Czech Republic) that quantifies the volume of water absorbed by the rock in situ through time. Among the advantages associated with the device is that water is applied only to the surface (this is important because case hardening is a surface / near surface phenomenon), and the instrument is graduated specifically for imbibition rates typical of porous rocks[5]. In trial runs of this test, absorption rates of recently exposed tuff surfaces were greater than for samples having more highly developed crusts. Rates for unaltered surfaces (Type 1) were essentially linear. For altered surfaces, absorption rates slowed as the experiment progressed; this suggests that the swelling of clays or mucilaginous films may play a role in reducing absorption for crusts in initial stages of development (Types 2-4), while for well-developed crusts with occluded pores, there appears to be initial filling of the available porosity followed by leveling off of the absorption rate (Table 2).

To evaluate comparative erosion resistance, investigators developed an in situ erosion test adapted from ASTM G76: Standard Test Method for Conducting Erosion Tests by Solid Particle Impingement Using Gas Jets. The method was adapted to the poorly consolidated tuff in terms of gas delivery pressures and blast media selected. The ASTM standard quantifies erosion in terms of mass loss, and measurements are made by weighing samples before and after each test run. Because tests at Bandelier were conducted in situ, the adapted test protocol includes a technique for collecting surface profiles before and after the test and calculating the areas between the profiles. Pilot test results indicate that sedimented silt / clay coatings

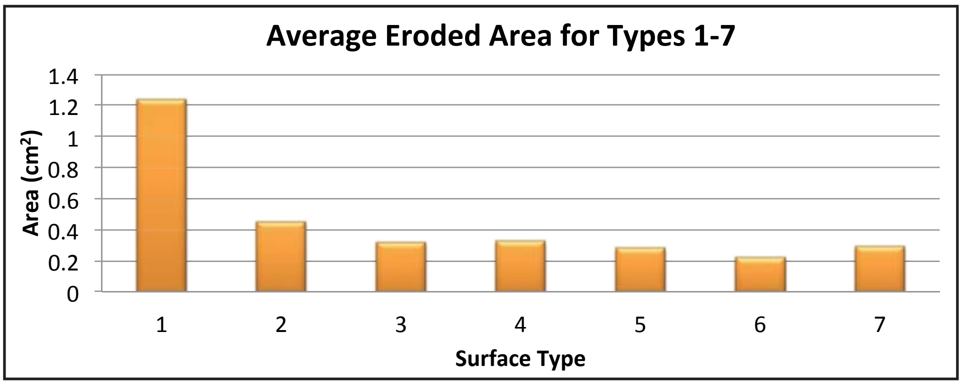


Table 3. Erosion was measured as the area between surface profiles collected before and after each test (Fig. 19), and average erosion areas were plotted for each surface type.

[5] *Sources of error include: 1) differences in surface temperature at each of the sample sites, perhaps resulting in significantly different rates of evaporation; and 2) there is currently no way to distinguish between the volume of water absorbed by surface biota and the volume absorbed by the rock. It is possible that a significant proportion of the water absorbed by surface biota is lost in transpiration.*

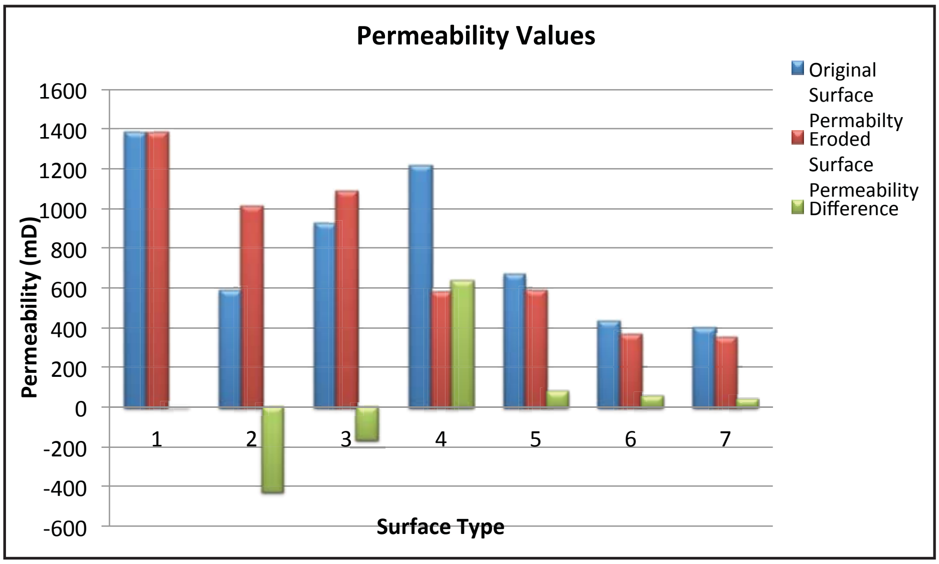


Table 4. Surface permeability values were collected for each sample with the sample surface intact. A second set of values was collected after eroding sample surfaces to remove sediments and biological material.

and the presence of even intermittent lichen cover enhance the erosion resistance of the tuff. There was frequently no measurable erosion of surfaces with highly developed case hardened crusts (Types 6 and 7) apart from the loss of surface sediments and biological material (Table 3). Since tests were run once at each test site, results document changes in surface profile regardless of the type of material (tuff vs. sedimented coatings/surface biota) lost. Running additional tests at each test site would tend to highlight the role of sedimented surface materials in the erosion resistance of the surface. For crusts in initial stages of development, it is expected that the rate of erosion would increase abruptly following the loss of the surface material; for well-developed crusts, erosion resistance is largely a function of hard secondary minerals precipitated in the near-surface zone, and it is expected that losses would tend toward 0 once sedimented and biotic surface crusts were removed.

In situ measurement of surface gas permeability is likely to be a useful measure of resistance to weather. It is expected that permeability decreases with increases in surface strength, and decreases proportionally with absorption rate. In pilot tests, surface gas permeability measurements were made using a handheld permeameter, the Tinyperm II, made by NER.[6] Measured permeability values for unaltered surfaces (Type 1) were greater than for surfaces with crusts, though the correlation to absorption and erosion resistance data is not very direct. Obtaining good coupling to the rock was not always possible, due to the fragility of some of the surface coatings, and testing of these fragile surfaces is likely to require adaptation of a dual-durometer coupler. For surfaces in the initial stages of crust development (Types 2 & 3), reductions in permeability are apparently largely a function of the materials accumulated on the surface (sedimented silt/ clay, biotic crusts), and permeability values for these samples were similar to Type 1 values once the surface coatings were removed. With more highly altered surfaces (Types 5-7), reductions in permeability seem more closely related to reductions in porosity in the near-surface zone, and removal of sediments / biological material from the surfaces of these samples had little impact on the measured values. The performance of surface Type 4 seemed clearly to mark a transition between the two groups, where removal of surface coatings resulted in a substantial reduction in surface permeability (Table 4).

A series of enzyme assays conducted in the laboratory correlate microbial activity to crust development. Activity of photosynthetic microbes, measured as chlorophyll content extracted by acetone, increased progressively with type, reaching an asymptote by tuff surface Type 6 or 7. Chlorophyll may represent activity by cyanobacteria as independent entities or as symbionts of lichens or actinobacteria. In contrast, saprophytic activity was greatest for intermediate Types 4 and 5. General saprophytic activity was measured as a maximum rate of β-glucosidase and general biological activity as phosphatase activity across a gradient of substrate concentrations.

[6] *Tinyperm II is a hand-held version of the Autoscan II, a surface gas permeameter that allows for spatially integrated measurements of gas permeability on specimen surfaces; the range of measurements is 0.01 to 10 darcys, and spatial coordinates on an x/y grid can be as small as 0.1mm (NER 2010).*

Collectively, these data support the hypothesis that there is a succession in microbial community on these surfaces. The greatest diversity of activity occurs at an intermediate stage that corresponds with a porous habitat and a balance between autotrophs and saprotrophs. Autotrophs colonize recently exposed rock surfaces. Exudation of oxalic acid dissolves glass in the near-surface zone, creating pore space for saprophytes. As autotrophs die, they are decomposed by saprophytes. However, eventually opal and other precipitated minerals occlude available pore space, reducing habitat for saprophytes and resulting in reduced microbial activity.

5. CONCLUSIONS

In the literature, lichens and other biota on culturally significant surfaces are typically discussed in terms of their biodeteriorative effects. Lichens, algae, and associated microflora excrete inorganic and organic acids that are effective chelating agents, and play a primary role in the biocorrosion of rock substrata (JONES & Wilson 1985; ADAMO et al., 1993; CHEN et al., 2000; ST. CLAIR & SEAWARD, 2004). Insoluble metal oxalate compounds, formed from cations released from substrate minerals and oxalic acid excreted by lichen mycobiants, frequently accompany colonization of rock surfaces and their occurrence is routinely interpreted as a measure of the biodeteriorative potential of a particular biocommunity (SEAWARD, 2004). The close relationship between substrate composition and the oxalate minerals that accumulate in lichen thalli is well documented (PURVIS et al. 1985; PURVIS 1996; WILSON et al. 1981). In addition, the dissolution of respiratory CO_2 contained in water held by lichen thalli can lower the pH at the substrate-thallus interface, accelerating the chemical weathering of the rock (SEAWARD et al., 1989; WIERZCHOS & ASCASO, 1996; JACKSON & KELLER, 1970).

For the Bandelier Tuff, however, improvements in bulk mechanical properties of the surfaces provide significant resistance to the erosional processes that threaten the archaeological resources of Frijoles Canyon. Even the presence of poorly indurated silt / clay coatings and intermittent lichen cover enhance erosion resistance and reduce absorption rates. Surface improvements occur as the result of two different processes: 1) colonization of outcrop surfaces by cyanobacteria, lichens and other biota cement wind-blown and water-transported particles to the rock face through secretion of sticky polysaccharides. The formation of dense networks of filaments infiltrate, reinforce, and stabilize the accumulated clay / silt coatings, and shield the loose ash in the bedrock tuff from wind- and water-driven actions that accelerate erosion, and; 2) excretion of organic acids by biotic crust constituents catalyze biogeochemical reactions that lead to dissolution of fine volcanic glass and cementation of the tuff surface by precipitation of secondary minerals in the network of interconnected pores. Both processes result in occlusion of pores at the surface, initially by the accumulation of clay / silt coatings and the presence of mucilaginous cyanobacteria in the surface crust, and eventually by the precipitation of secondary minerals (principally opal, calcite, and clay) in the near-surface pore space of the tuff. As crusts develop, imbibition rates at the surface gradually decrease, limiting the potential for additional hydrolytic reactions. At the same time resistance to erosion increases, initially due to the protective buffer provided by sedimented coatings and the surface biota that colonize them, but eventually as the result of deposition of secondary minerals that are much harder than the poorly consolidated glass.

The impacts of biological activity on the rock surface are paradoxical in the sense that both deteriorative and protective effects are produced. However, the protective effects appear to outweigh the biodeteriorative effects in terms of surface durability[7]. Where the crusts are damaged, erosion occurs at accelerated rates, resulting in losses of many cubic centimeters over the course of a few decades (based on comparative analysis of images produced in the early years of archaeological documentation of the canyon with more recent images of the same features / sites). The most well developed crusts, by comparison, are thousands of years old. Furthermore, the hydrolytic processes catalyzed by biotic crust constituents are self-limiting in a sense. Microbial populations initially thrive as they derive essential nutrients from the dissolution reactions they catalyze in the volcanic ash, but biological activity eventually declines as precipitation of secondary minerals

[7] *Other researchers report similar benefits conferred by lichen / microbe cover on other types of rocks (Mottershead and Lucas, 2000; Viles and Pentecost, 1994; Arino et al., 1995). Algal layers on sandstone formations in Western Australia are thought to perform a consolidating function, for example. Cryptoendolithic lichen growths have been identified as weathering rinds on some sandstones. With relatively soluble rocks, like Spanish gypsum, lichen cover results in reduced rates of erosion and a distinct surface morphology resulting from the development patterns of the lichen cover.*

decreases porosity in the near-surface zone and limits access to new sources of nutrients. Initial experiments suggest that microbial demand for organic and inorganic sources of $PO4^{-3}$ gradually exceeds supply as succession progresses. This is correlated positively with the concentration of chlorophyll. A $PO4^{-3}$ deficit develops in older surfaces with well-developed crusts where the pore space has been occluded by secondary minerals. As pore space and phosphorus become less available, colonization by additional cyanobacteria and lichens is limited.

In the initial stages of development, the crusts that form on vertical and subvertical outcrop surfaces of the Qbt1g function analogously to biological soil crusts on non-cohesive soils in arid and semi-arid climates. Soil crusts are almost universally effective in reducing surface erosion associated with wind and water. Well-developed crusts, with lichens and mosses, offer 2 to 130 times greater resistance to erosion than soils with less well developed crusts (BELNAP et al., 2001). With respect to water erosion, lichen cover prevents direct impact of raindrops on soil surfaces, and microfilamental reinforcement of the upper soil layers and the cementing action of extracellular polysaccharide compounds exuded by fungi, algae, and cyanobacteria help to contain soil particles at the surface (SCHULTEN, 1985; BELNAP & GARDNER, 1993; TISDALE & OADES, 1982). Additionally, rough surface microtopographies reduce the energy of runoff and the transport of sediment (BELNAP, 1995; BLACKBURN, 1975). By binding soil particles together, crusts effectively increase the threshold friction velocities of soils, making them more resistant to wind erosion (BELNAP & GILLETTE, 1997, 1998; LEYS & ELDRIDGE, 1998; BELNAP & GARDNER, 1993; ELDRIDGE & GREENE, 1994).

Like biological soil crusts, the biotic crusts that form on the Bandelier Tuff are easily disturbed; cyanobacterial and microfungal filaments become brittle when dry, and are easily crushed (BELNAP & LANGE 2001: 342). South-facing canyon walls (where the cavates are excavated) are pockmarked with damage sites resulting from loss of the crusts (as the result of falling debris, for example) and the effects of wind and water erosion on these unprotected surfaces. Many of these, because of their proximity to archaeological resources carved in the rock, result in the loss of cultural material. Soil crust recovery can, in some cases, be accelerated by inoculation (FAUST, 1970 & 1971; see also, LEWIN, 1977; TIEDEMANN et al., 1980; ASHLEY & RUSHFORTH, 1984; ST, CLAIR et al., 1986; BELNAP, 1993; BUTTARS et al., 1998), and it seems possible that minimal stabilization of eroding tuff surfaces may be promoted by the application of silt/clay washes to the bare tuff. Given the prevalence of surface biota on the rock face, inoculation may occur without additional intervention once the surface has been minimally stabilized in this way. Our hope is that better understanding of case hardening will at least provide a counterpoint to design responses from the heritage community that are primarily focused on lichen removal, and may lead to the development of such low-impact interventions for stabilization of rapidly eroding areas that currently threaten these resources. This research represents a departure from traditional studies that explore the biodeteriorative effects of biotic crusts on rock surfaces, and may provide a new model for understanding the interaction of microflora with poorly consolidated rocks. A better understanding of the complex interaction between biotic crusts and these landscape-scale monuments, including the role of biotic crusts in improving the competence of porous and unconsolidated rock, is likely to be useful in the preservation and management of other troglodytic and rock art sites.

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